Mercury Oxidation across SCRs in Coal-Fired Power Plants

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Mercury Control Technology R&D Program Review

Pittsburgh, PA

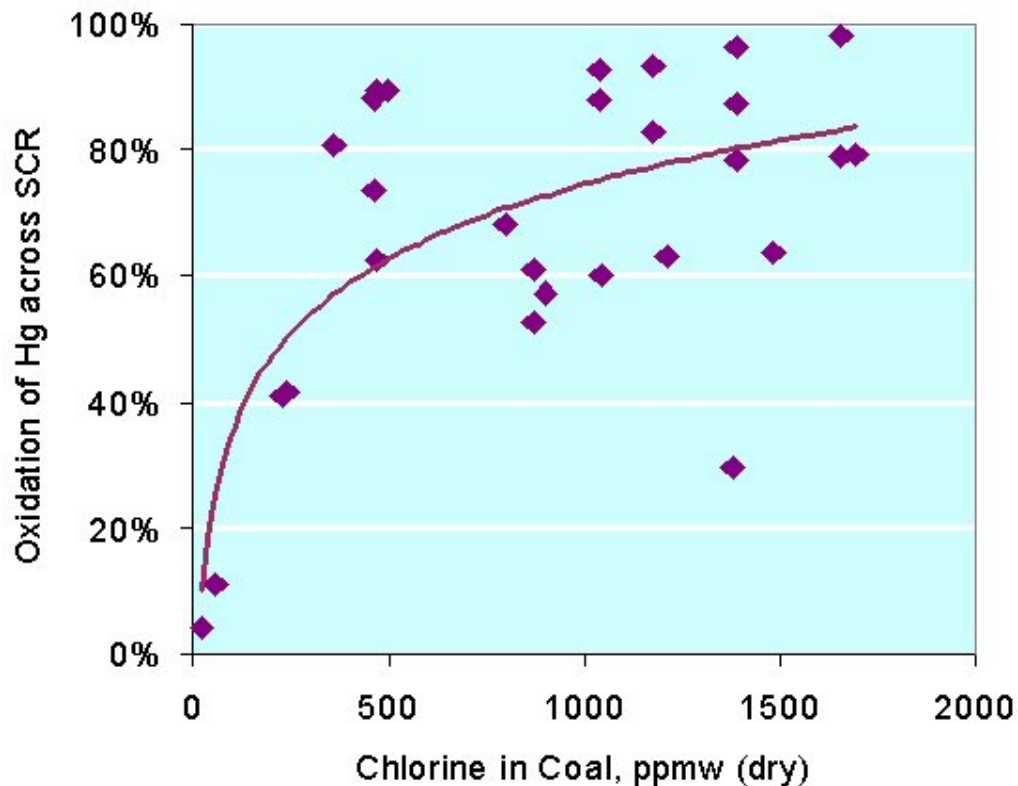July 12014, 2005

Presentation Outline

➤ Rationale for model

➤ Model specifics

➤ Validation

➤ Summary

Acknowledgements:

DOE/NETL, EPRI, Argillon

AEP (slipstream reactor support)
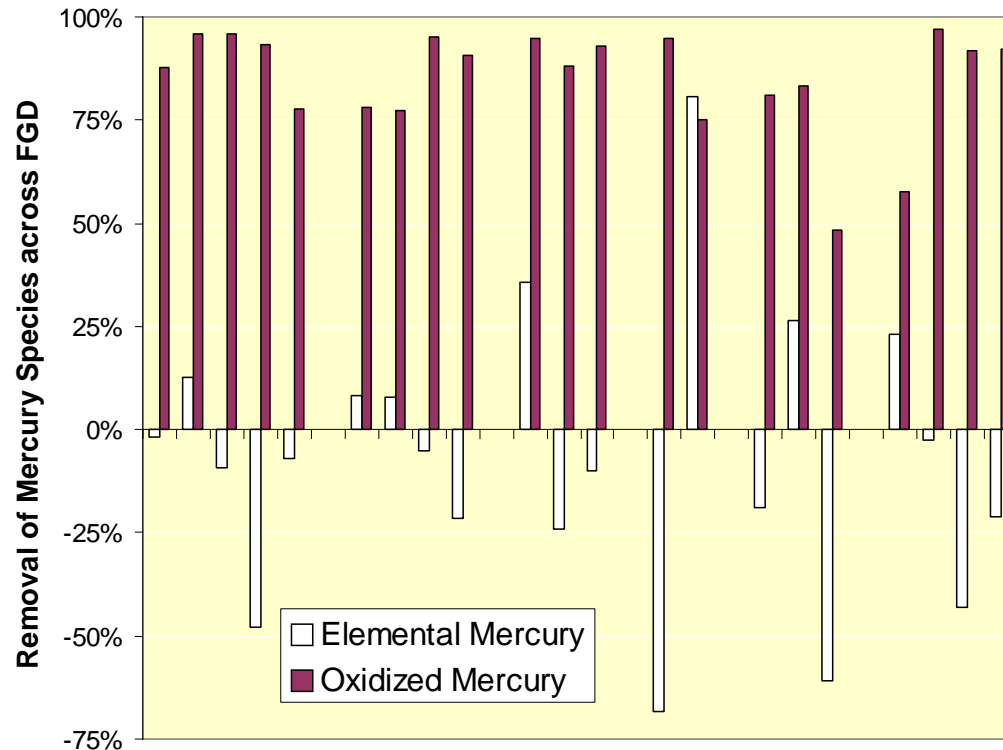
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Hg⁰ Oxidation Across SCRs

- Full-scale data
- SCRs oxidize mercury
- Chlorine content of coal influences oxidation

Mercury Speciation in Combustion Systems

Source: ICR data

- ➢ *Wet scrubbers remove:*
  - ➢ *~90% of Hg^{+2}*
  - ➢ *<25% of Hg^0*
- ➢ *SCR + scrubber as control device?*

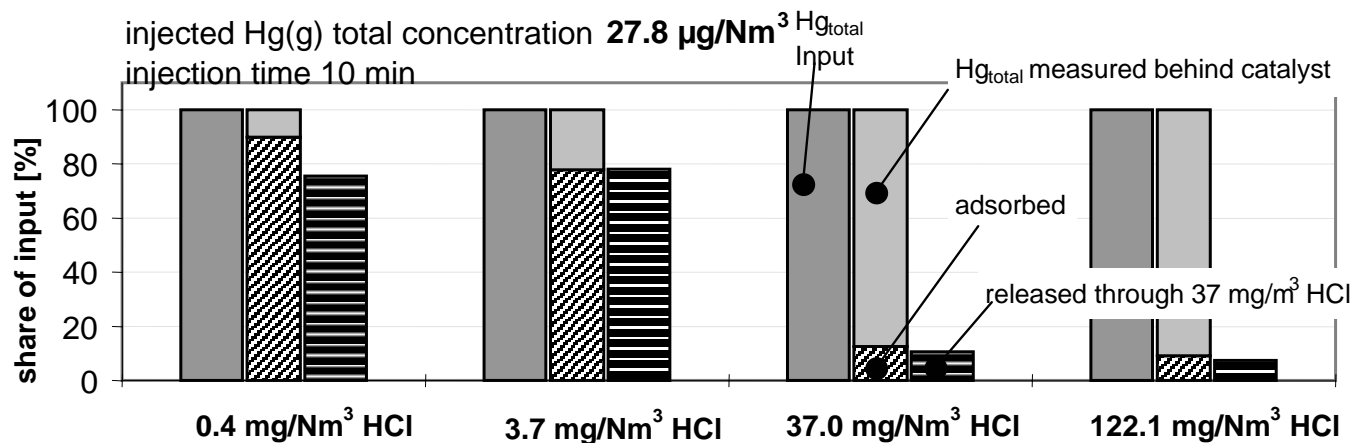# Review of Lab, Pilot and Full-Scale Data

➢ Laboratory data

– Effects of temperature, ammonia, HCl, space velocity

– Adsorption of Hg^0

➢ Pilot data

– Effects of temperature, ammonia, space velocity, flue gas

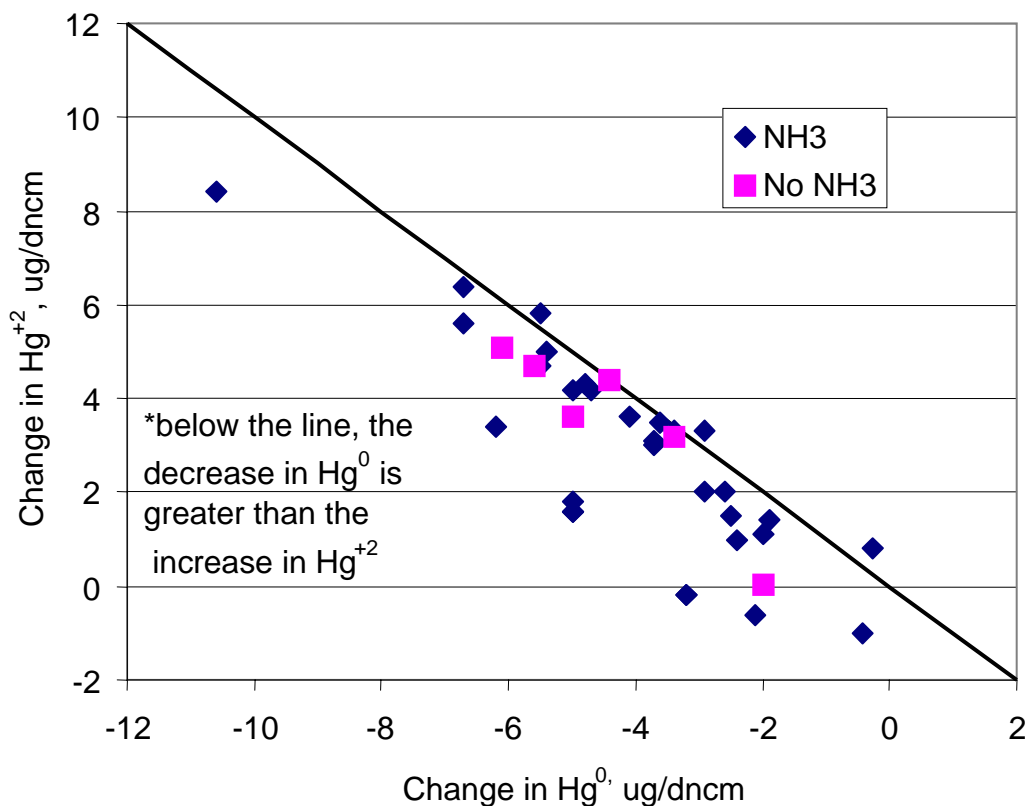– Transients

SCR Catalysts Adsorb Hg^0

➢ Lab data from Hocquel et al.

injected Hg(g) total concentration **27.8 µg/Nm³** Hg_{total} Input
injection time 10 min

Hg_{total} measured behind catalyst

adsorbed

released through 37 mg/m³ HCl

share of input [%]

100
80
60
40
20
0

0.4 mg/Nm³ HCl   3.7 mg/Nm³ HCl   37.0 mg/Nm³ HCl   122.1 mg/Nm³ HCl
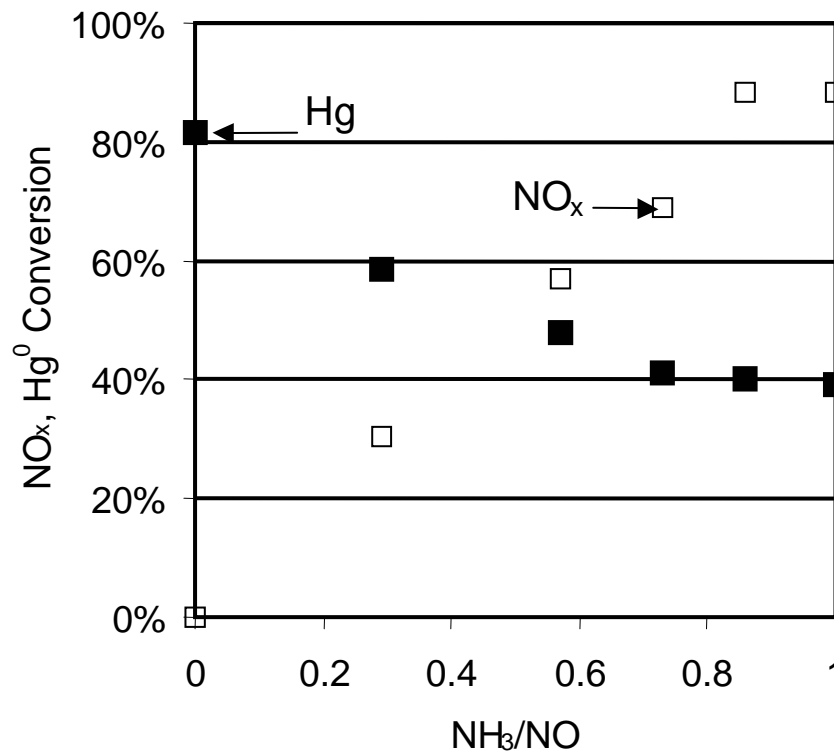
➢ Net adsorption of Hg^0 by catalyst in ten-minute experiments

➢ Amount of Hg^0 adsorbed decreased with increasing HCl concentration

➢ *HCl interferes with Hg^0 adsorption?*

Adsorption of Hg

➢ Adsorption of Hg observed in full-scale measurements?

➢ Yes, in some cases loss of Hg^0 higher than gain of Hg^{+2} across SCR

Chart: y-axis "Change in Hg^{+2}, ug/dncm" (from -2 to 12), x-axis "Change in Hg^{0}, ug/dncm" (from -12 to 2)

Legend: ◆ NH3 ■ No NH3

*below the line, the decrease in Hg^0 is greater than the increase in Hg^{+2}
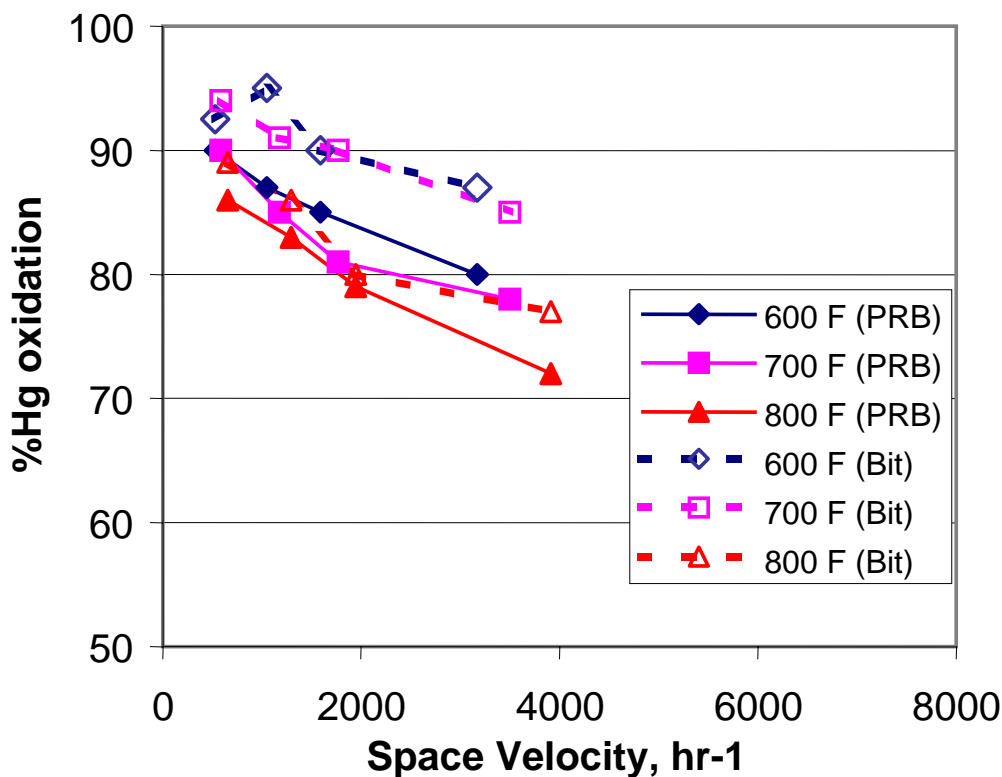
Ammonia Affects Hg⁰ Adsorption

> Slipstream data (Machalek et al.)
> Pilot-scale SCR with PRB flue gas
> Ammonia decreased Hg⁰ oxidation

Ammonia Affects Hg⁰ Adsorption

Catalyst C2
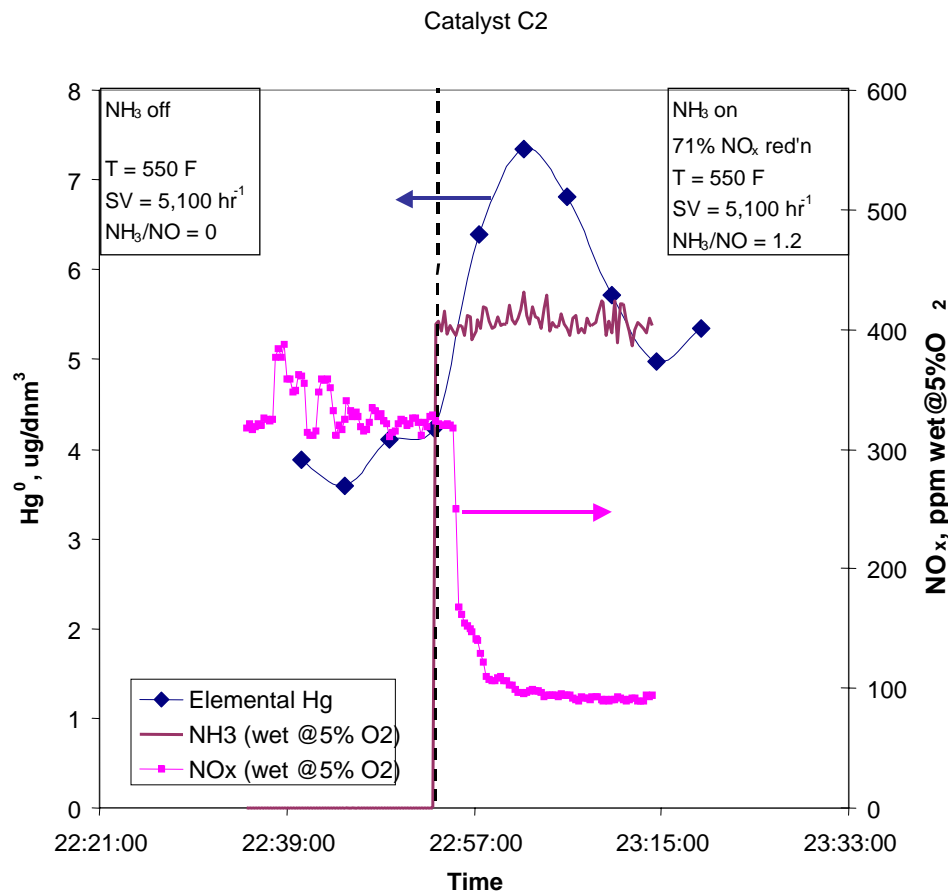
- ➢ Transient from Rockport
- ➢ Turning ammonia on causes spike in Hg^0
- ➢ *NH_3 interferes with Hg^0 adsorption*

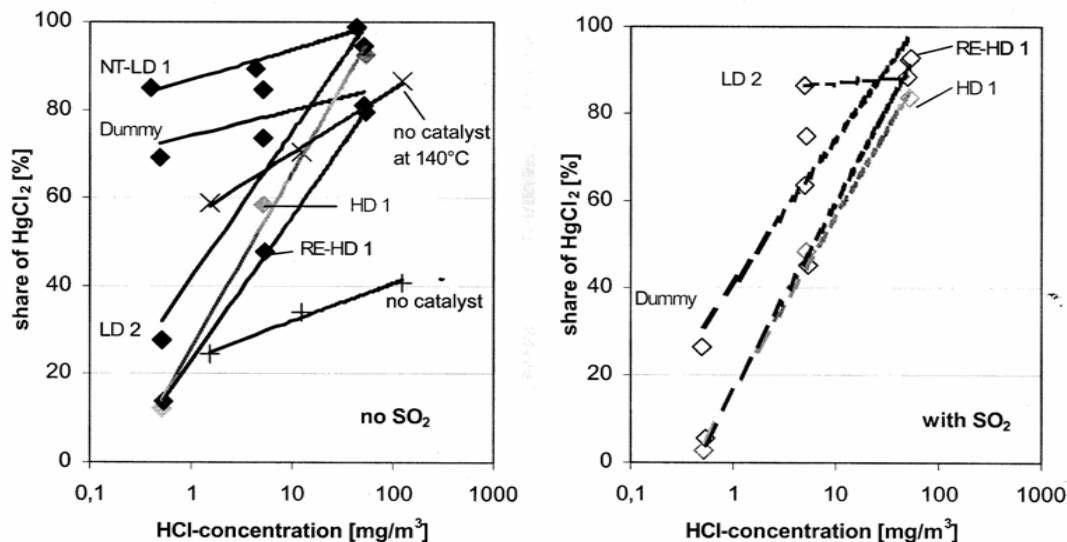# Temperature Affects Oxidation
Pilot-Scale

- Pilot-scale SCR (Richardson et al.)
- Oxidation decreases when temperature increases

Legend:
- 600 F (PRB)
- 700 F (PRB)
- 800 F (PRB)
- 600 F (Bit)
- 700 F (Bit)
- 800 F (Bit)

X-axis: Space Velocity, hr-1
Y-axis: %Hg oxidation

HCl Promotes Hg^0 Oxidation

- ➢ Lab data from Hocquel et al.

- ➢ Increasing HCl content of simulated flue gas increases oxidation
- ➢ Little effect of SO$_2$
- ➢ *HCl reacts with adsorbed Hg^0 or is itself adsorbed?*

Computational Approach

➢ Goal: Predict Hg^0 oxidation across SCR catalyst

➢ Observations:

– Hg not at equilibrium at SCR exit

– Hg adsorption and oxidation sensitive to ammonia concentration

– Hg oxidation affected by concentration of chlorine species (largely HCl)

Hg Speciation at SCR Temperatures

Inlet
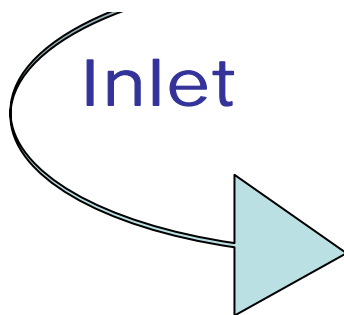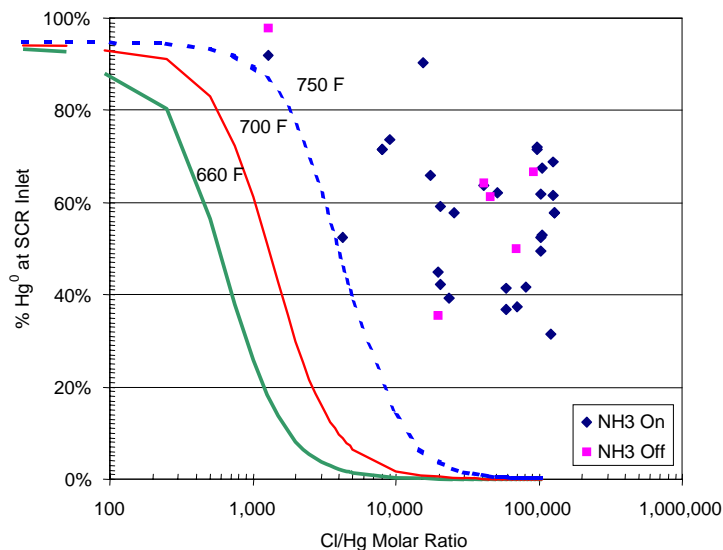
➢ Hg not at equilibrium at SCR exit
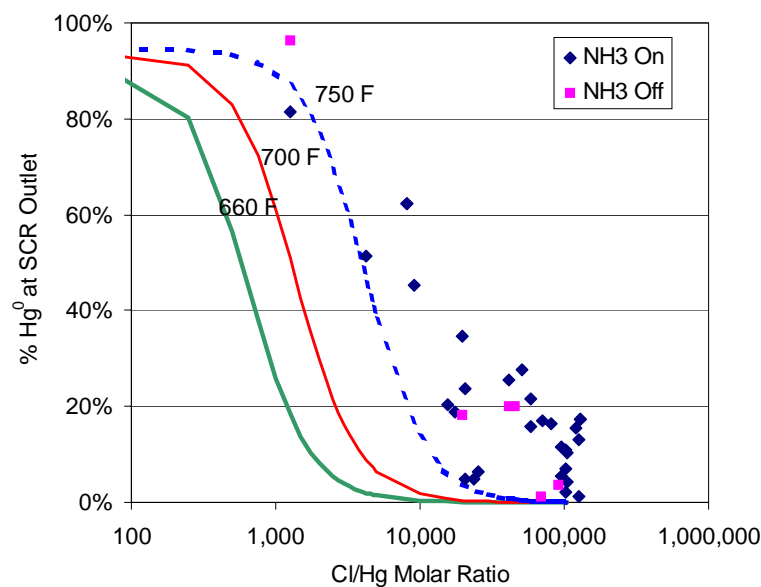

Outlet

Computational Approach

➢ Hg adsorption and oxidation sensitive to ammonia concentration

➢ Need to model distribution of ammonia in catalyst:
  ➢ First-order NO kinetics
  ➢ Mass transfer:
    ➢ Along channel
   ➢ Within porous catalyst

Computational Approach

➢ Hg adsorption and oxidation sensitive to ammonia concentration

➢ Distribution of NO along catalyst channel:

$$y_i(z) = y_{i,o} \exp\left[-\left(\frac{Pz}{uA}\right) \frac{1}{\dfrac{1}{k_m} - \dfrac{1}{\sqrt{D_i^e ka}}\left(\dfrac{e^{-2\Phi}+1}{e^{-2\Phi}-1}\right)} \right]$$

➢ Distribution of NH_3 follows stoichiometry of NO reduction

NO Reduction Model
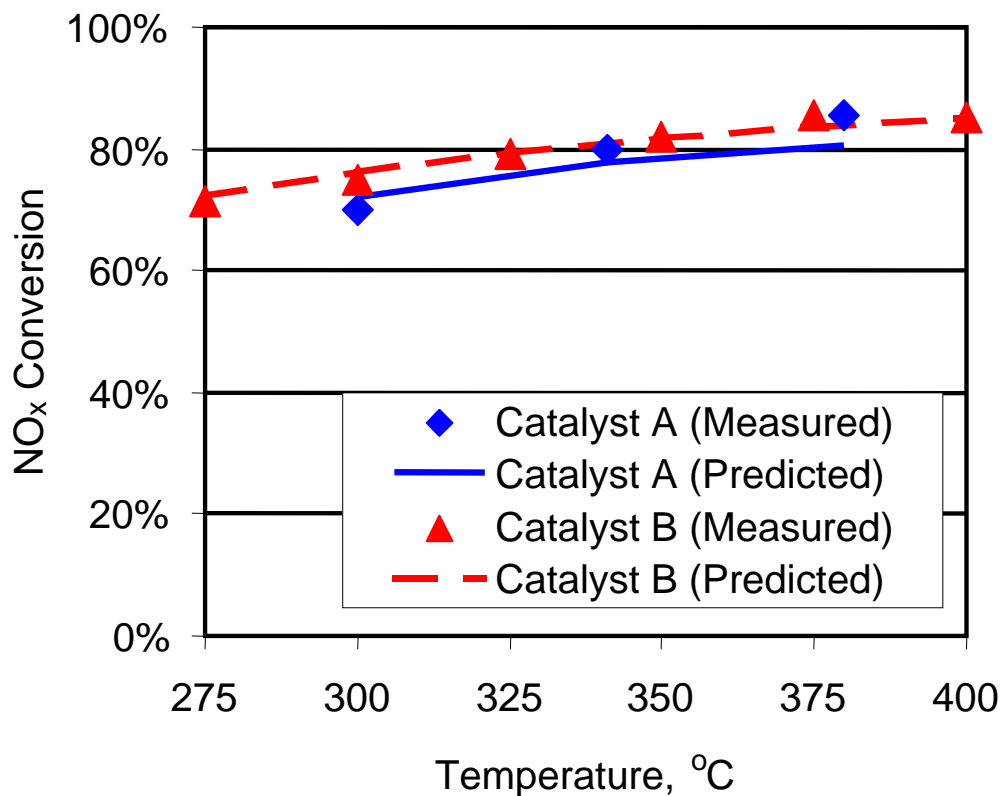
➢ Lab data from Beeckman and Hegedus

➢ Two monolith catalysts, simulated flue gas

NO Reduction Model
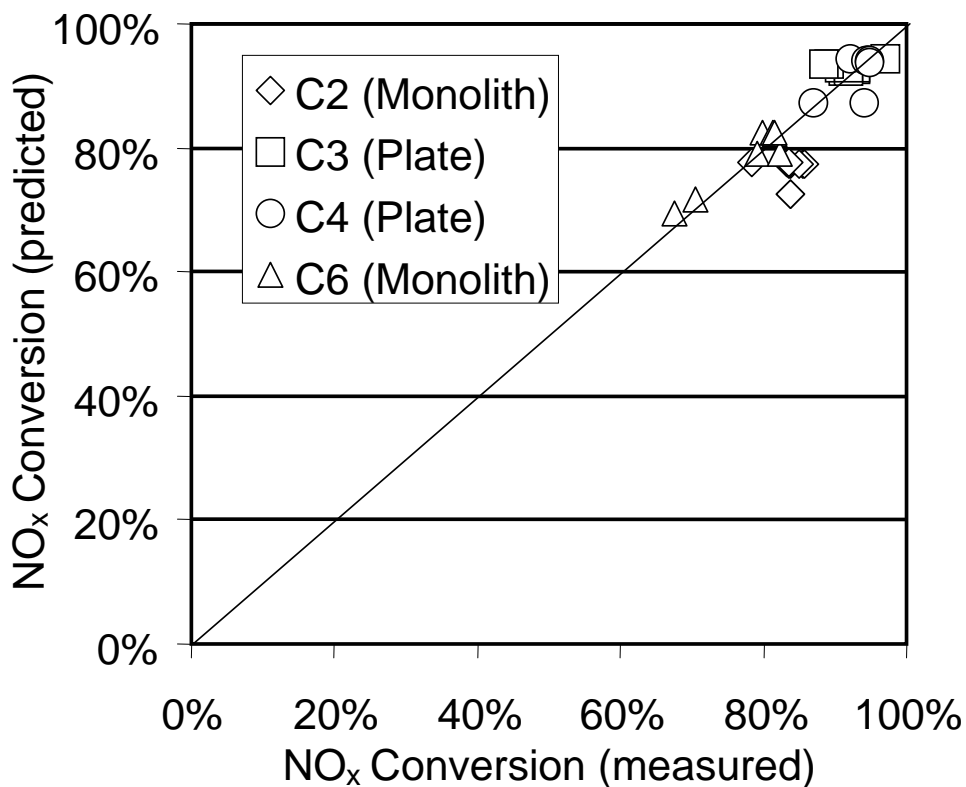
➢ Slipstream data from Rockport Unit 1
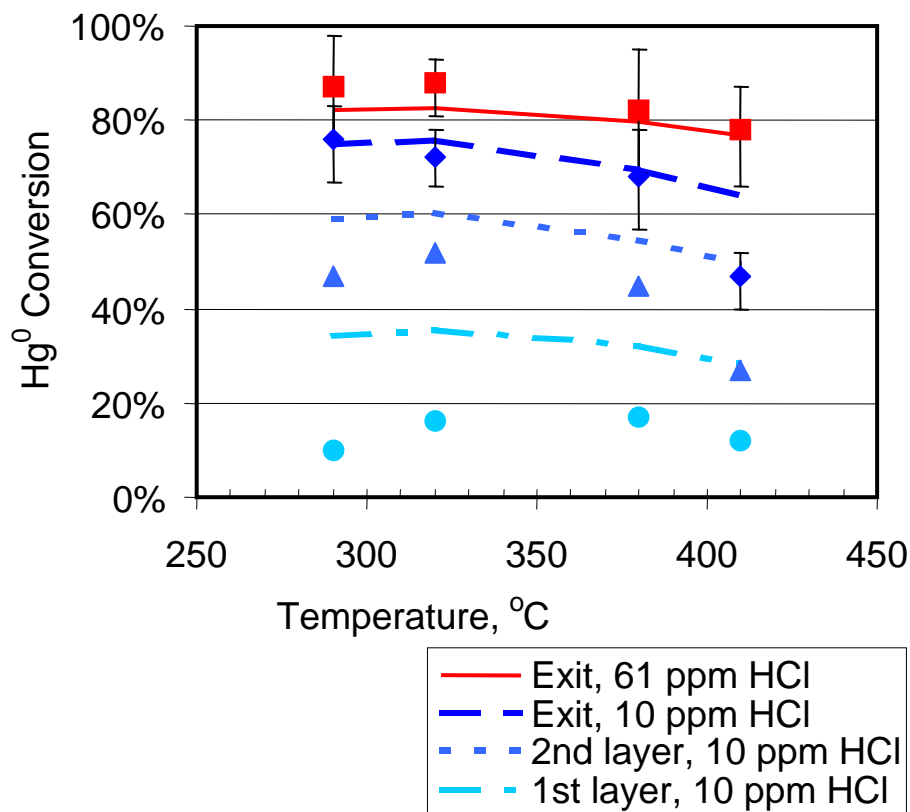
➢ Two monolith catalysts, two plate catalysts

Computational Approach

➢ Hg oxidation affected by concentration of chlorine species (largely HCl)

➢ Reaction of adsorbed Hg^0 with $HCl_{(g)}$

➢ Competition with NH_3 for surface sites

➢ Rate of oxidation:

$$r = \frac{k_o e^{-E/RT} K_{Hg} \, y_{Hg} \, y_{HCl}}{\left(1 + K_{NH_3} \, y_{NH_3} \right)}$$

Hg⁰ Oxidation Model

Hg^0 Conversion vs Temperature, ^{o}C

Legend:
- Exit, 61 ppm HCl
- Exit, 10 ppm HCl
- 2nd layer, 10 ppm HCl
- 1st layer, 10 ppm HCl

- ➤ Lab data of Hoquel
- ➤ 3 layers of commercial plate catalyst
- ➤ Simulated flue gas
  - – Two HCl levels
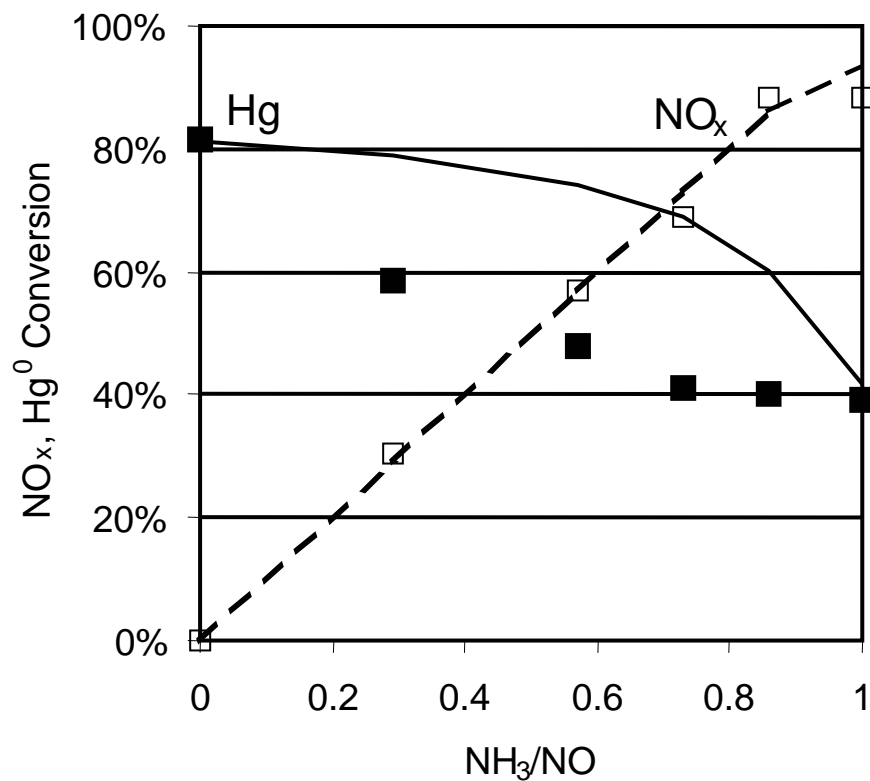- ➤ Hg, NO measurements made in between layers

Hg⁰ Oxidation Model
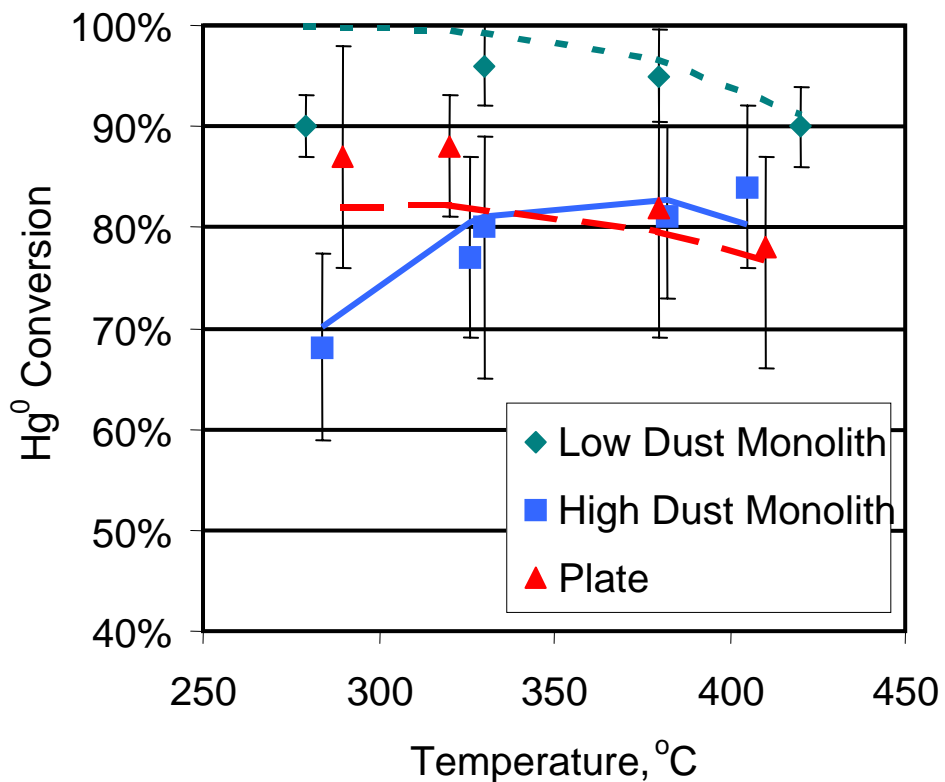
- Lab data of Hoquel
- Commercial plate and monolith catalysts
- Simulated flue gas
- No NO measurements report for monolith
- Effects of mass transfer, catalyst design

Hg⁰ Oxidation Model

> Slipstream data (Machalek et al.)
> Pilot-scale SCR with PRB flue gas
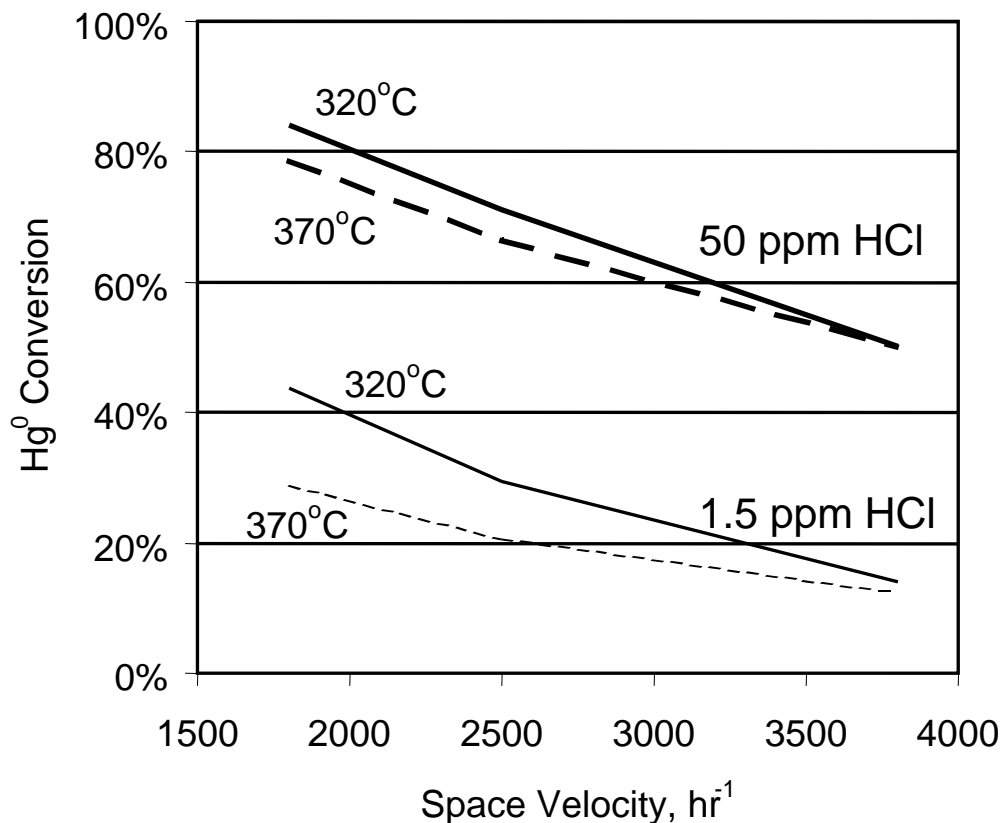> Ammonia decreased Hg⁰ oxidation

Hg⁰ Oxidation Model

	SV, hr^{-1}	NH$_3$/NO	Avg T, ^{o}C	Observed			Pred.
C2	5,037	1.7	321	6%	$\pm$	10%	13%
(Monolith)	5,051	0.0	326	61%	$\pm$	13%	44%
C3	1,927	2.1	327	4%	$\pm$	22%	87%
(Plate)	2,439	0.0	333	83%	$\pm$	5%	80%
C4	3,992	1.2	347	52%	$\pm$	7%	57%
(Plate)	2,353	0.0	334	83%	$\pm$	10%	81%
C6	3,915	1.2	337	10%	$\pm$	13%	34%
(Monolith)	2,219	0.0	325	75%	$\pm$	5%	76%

➤ Data of from slipstream reactor, Rockport 1

➤ Trends with and without NH$_3$

Hg⁰ Oxidation Model

> ➤ Example, monolith catalysts
> ➤ $NH_3/NO=0.9$
> ➤ Effects of SV, chlorine, temperature

Summary

➢ Model of Hg^0 oxidation across SCR catalysts fits laboratory and slipstream data

– Activation energies fixed; pre-exponential factors related to NO reduction

– Explains non-linear temperature-dependence

– Effects of ammonia, HCl content, space velocity and catalyst design included